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Synthesis of microcapsules for carbon capture via needle-based droplet microfluidics

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Abstract

"Off-the-shelf" devices have attracted much consideration lately, especially in emulsions production in droplet-based microfluidics. While many simple and cost-effective designs have been proposed and demonstrated, the functionality of these purported simple devices has been questioned, especially in emulsions generation for commercial scale. In this work, a simple needle-based device was used in the production of functional core-shell microcapsules of uniform sizes, typically in the range of 600 to 720 μm, and shell thickness of 20 to 110 μm, and C.V of 0.97 to 3.0%. These core-shell microcapsules are a new form of carbon capture materials, with carbon solvent encapsulated in thin polymeric shell. The microcapsules synthesized were subjected to absorption-desorption tests. This work has successfully demonstrated the use of off-the-shelf microdevice and its reliability for the production of functional microcapsules.

Keywords: core-shell; microcapsules; microdevices; carbon capture

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1. Introduction

Droplet-based microfluidics has recently received great attention in emulsions fabrication [1]. Emulsions of different sizes and morphologies can be generated and manipulated in micro-devices of different geometries. Conventional methods of droplets synthesis such as emulsion polymerization, suspension polymerization or evaporation-induced consolidation, usually do not guarantee high monodispersity, whereas microfluidic approach allows precise control over size, shape, and morphologies of microdroplets [2]. Emulsions are also used as templates for the production of functional microparticles, such as Janus microparticles, core-shell microemulsions, and hybrid microparticles which have been developed with the advances of microtechnologies [3, 4].

There have been extensive studies conducted on droplet microfluidic device fabrication, device geometries and break-up mechanisms as yet [5-7]. Photolithography and soft lithography are the two most common microfabrication methods, which involve arduous steps of transferring designs. For emulsification via droplet based microfluidics, capillary microfluidic devices are better as they are more rigid and are able to withstand organic solvents. Yet this fabrication method is technically challenging, and reproducibility in fabrication is more difficult than with lithographically produced devices. Lately, the idea of "off-the-shelf" device has attracted much consideration, microdevices or droplet generators assembled using commercially available components as alternatives to designed microdevices with complicated fabrication processes. Some of these off-the-shelf components include dispensing needles, laboratory tubing and tiny plastic fittings. Benson et al. [8] improvised a glass capillary device which can be disassembled and reconfigured for multiple use with flangeless ferrules, screws and PVC tubing, while Steinbacher [9] reported simple T-junction device and flow-focusing device by puncturing dispensing needles into tubing in which the continuous phase flows. Production of single and double emulsions has also been demonstrated on microfluidic devices made from patterned coverslips and microscope glass slides [10]; however, researchers have questioned the functionability of these purported simple devices in generating emulsions, especially for commercial formulations such as drug synthesis. Li et al. [11] reported the assembly of yet another off-the-shelf microdevice with flexible designs. As the device is mainly composed of dispensing needles of different sizes, and assembled with mini tee- and cross-links, it will henceforth be termed as needle device. By altering the configuration of the device, monodispersed single droplets and double droplets with multiple cores with high controllability are generated. In comparison, the design of the needle device is more robust and may be suitable for use in production of emulsions at industrial quantities.

Notably there has been extensive development of functional polymeric microparticles synthesized via droplet-based microfluidics for various applications, such as drug delivery and cell encapsulations [2, 4]. By regulating channel geometries and flow rates, emulsions can be compartmentalized into containing several different domains which can be used as microcarriers of multiple ingredients. For instance, core-shell structure capsules can be used to carry drugs, which when triggered by different stimuli, release the active ingredients within [12]. In this paper, "off-the-shell" needle devices are used to synthesize functional core-shell microcapsules for carbon capture. This work is to demonstrate the practicability of needle device in droplet fabrication.

Nomenclature

D	size of droplet
Q_i	flow rate of inner phase
Q_m	flow rate of middle phase
Q_o	flow rate of outer phase
$C.V.$	coefficient of variation

2. Microcapsules for carbon capture

Most recently, interest has arisen in using microfluidic-synthesized functional materials in pollutant separation and removal such as the use of chitosan microspheres for removal of copper ions [13, 14] from wastewater and silicon microcapsules for gas absorption [15]. Aines et al. [16] first reported on encapsulated solvents in silicone

microcapsules for carbon capture, of which the silicone shell allows the permeation of CO_2 into the liquid core containing carbonate solutions. The microscopic double emulsions are a new form of carbon capture materials considered to have the desirable characteristic features of both solid and liquid sorbents, and these microcapsules were produced via a microfluidic double glass capillary device. The microcapsules were subjected to multiple absorption-desorption cycles and have displayed high CO_2 as compared with sorbents of equivalent mass. The microcapsules can be regenerated to release highly purified CO_2 and to be used again. The advantages of these microcapsules over conventional solvent-based carbon capture using amine solution such as Monoethanolamine (MEA) is that it allows easier handling of other prospective solvents for instance carbonate solutions, ionic liquids (ILs), and CO_2-binding organic liquids (CO_2BOLs) that could be highly viscous, corrosive, or difficult to handle, by encapsulating them within a protective yet permeable shell layer.

Stolaroff et al. [17] also subsequently studied other promising core and shell materials respectively, and developed two custom formulations of shell materials, silicone with thiol-ene curing mechanism and a UV activated acrylate material, 3-[Tris(trimethylsiloxy)silyl]propyl methacrylate (SiTRIS) , both of which are promising shell materials with comparable CO_2 permeability. They have also replaced the liquid core solvents with proprietary ionic liquids and phase-changing ionic liquid, successfully generating thiol-ene silicone capsules with core solvents of Koechanol/water and P_{2222}benzimidazole/water, and SiTRIS capsules containing ionic liquid NDIL0231/water.

To the best of our knowledge, there are currently three research groups working on the synthesis of microcapsules for carbon capture via microfluidic approach. Two groups have demonstrated the production of microcapsules with double glass capillary devices and have opted for photopolymerisable silicone rubber Semicosil 949 UV as shell material [15, 18]. While Vericella et al. mainly worked on formation of different capsules for carbon capture, Nabavi et al. [18] investigated other parameters affecting the formation and stability of the microcapsules, such as the effect of stabilizers, shell photopolymerization and effect of osmotic imbalance on the morphology of capsules. Wang et al. [19] developed a 3D non-planar polydimethylsiloxane (PDMS) device for encapsulation of nanoparticle organic hybrid materials (NOHMs) as the core solvent. In this paper, PDMS which is conventionally used for the fabrication of microdevices, is selected as the shell material. By utilizing its high gas permeability, especially to CO_2 [20], coupled with a modified off the shelf fabrication method, microcapsules containing carbon solvent are synthesized. This research offers an alternative with quick fabrication steps and simple encapsulation process. The result has shown compatible quality as the microcapsules produced by the other research groups.

Table 1. A summary of work on microcapsules for carbon dioxide by different research groups.

Reference	Stolaroff et al. [15-17]	Nabavi et al. [18]	Wang et al. [19]
Device	Double glass capillary device		3D non-planar PDMS microdevice
Research focus	• Screening of suitable materials for capsules formation • Formulation of new capsules shell materials • Capsule formation with different core solutions • Capsules CO_2 absorption studies	Study on parameters affecting droplets stability • Amount of stabilizers • Concentration and/or pH of alkaline core solutions • Osmotic imbalance between core and storage solution • UV irradiance on shell polymerization	• Development of PDMS microfluidic device. • Use of non-aqueous carbon capture solvent as core solvents, namely nanoparticle organic hybrid materials (NOHMs)

3. Materials & Methods

Sylgard 184 PDMS elastomer kit consisting of silicone elastomer base and curing agent was obtained from Dow Corning. Potassium carbonate, ethylene oxide-propylene oxide-ethylene oxide triblock copolymer surfactant (Pluronic F108) and thymol blue were all purchased from Sigma-Aldrich while poly(vinyl alcohol) (PVA, 87-89% hydrolysed) was purchased from Aladdin Chemistry Co. Ltd. All chemicals were used as received. Needle gauges

of different sizes and lengths, UV-curing adhesive (Kafuter K-302), UV-LED torch (365 nm, 5 W), plastic fittings and silicone tubes for the assembling of needle devices were all easily obtained from Taobao online shopping website.

3.1. Fabrication of needle device

The needle device for the synthesis of core-shell capsules was an assembly of dispensing needle gauges of different sizes, plastic tee and cross links, and polypropylene fittings, based on previously reported work by Li et al. [11]. Three different sizes of stainless steel dispensing needles were used (27-21-19G), with the narrowest and longest for the inner (dispensing) phase, to the widest for the outer (continuous) phase. The device was made up of two sections, a coaxial section where the middle phase was channeled in through a tee link, and a flow-focusing section where the outer phase was delivered through a cross link, as illustrated in Figure 1(b). The dispensing needles were aligned and placed within the tee and cross links, and the individual parts of the needle device were assembled together using UV-curing adhesive. A glass capillary was attached to the dispensing needle at the collection outlet to better observe droplet formations.

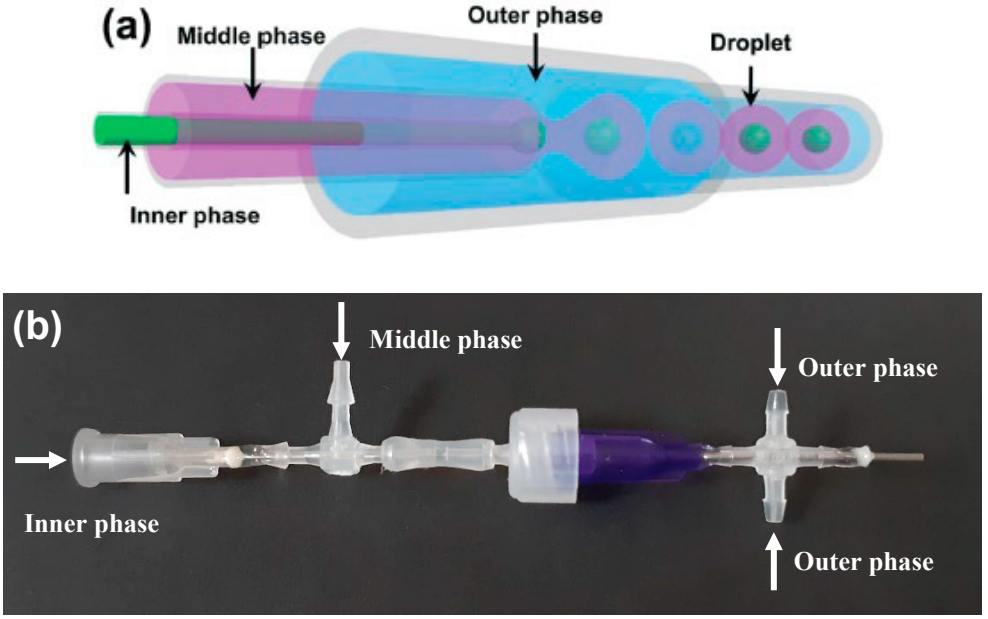

Fig. 1. (a) Schematic illustration of the generation of double droplets via needle device by Li et al. [11]; (b) Device assembly with three different sizes of needles: 27G (ID: 210 ± 10 µm, OD: 410 ± 10 µm), 21G (ID: 510 ± 10 µm, OD: 820 ± 10 µm) and 19G (ID: 750 ± 10 µm, OD: 1000 ± 10 µm).

3.2. Synthesis of microcapsules

PDMS base and curing agent were mixed at a typical 10:1 ratio by weight and degassed for 30 minutes to remove air bubbles induced during mixing. 3 wt% aqueous K_2CO_3 was prepared as the inner phase. The outer phase is a mixture of surfactants F108 and PVA with deionized water. All the solutions prepared were transferred into syringes to be mounted onto syringe pumps. Core-shell microcapsules of PDMS shell and potassium carbonate core were synthesised with the needle device connected to syringes mounted on three syringe pumps (LSP01-2A, LSP01-2B and LSP10-1B). Flow rate for each of the phases ranged from 1 to 30 µL min^{-1} for inner and middle phases, and 100 to 400 µL min^{-1} for the outer phase. The microcapsules synthesised successfully were collected in a beaker and hot

water was poured onto the microcapsules for quick curing. This step was repeated until the shell of the microcapsules have completely cured. The microcapsules were then transferred and kept in potassium carbonate solution isotonic to the liquid solvent of the microcapsules core to minimize osmotic swelling and rupture. The microcapsules appeared to be stable even after being kept for 6 months.

3.3. Characterization and absorption-desorption test of microcapsules

Optical images of the microcapsules were obtained using Phantom Camera mounted on top of a microscope, and image analysis was carried out using ImageJ software. Thymol blue, a pH indicator, was added to aqueous potassium carbonate solution which formed the core of the microcapsules. Prior to the absorption-desorption test, the microcapsules were removed from the solution and dried, before being loaded onto mesh and into a customized apparatus for testing.

4. Results & Discussion

In the same as how droplets are formed in other microfluidic devices, droplets are formed through the shearing of the dispersed phase by the continuous phase in the needle device. While Li et al. immersed the dispensing needles in octadecyltrichlorosilane (OTS) solutions followed by heat-treatment at 80°C, in this work, the needles were not subjected to any treatment prior to use, and there has not been any unusual flow phenomenon observed during droplet formation. For the synthesis of double emulsions, the needle device above is an assembly of three differently sized needle gauges (27G-21G-19G) with both coaxial and flow-focusing configuration. The needle device can be easily assembled within 15 minutes. The selection of the size of dispensing needles for each of the phases would affect the size of droplets produced. The size of the droplets can also be manipulated by adjusting the distance between needles, and the flow rates of each of the phases. The size of droplets, D increases in size with an increase in the inner and middle phase flow rates, Q_i and Q_m respectively, and the opposite was observed when the outer phase flow rate, Q_o is increased, as shown in Figure 2. By using this device configuration, the sizes of microcapsules produced are typically in the range of 600 to 720 µm, and shell thickness of 20 to 110 µm, and *C.V.* of 0.97 to 3.0%.

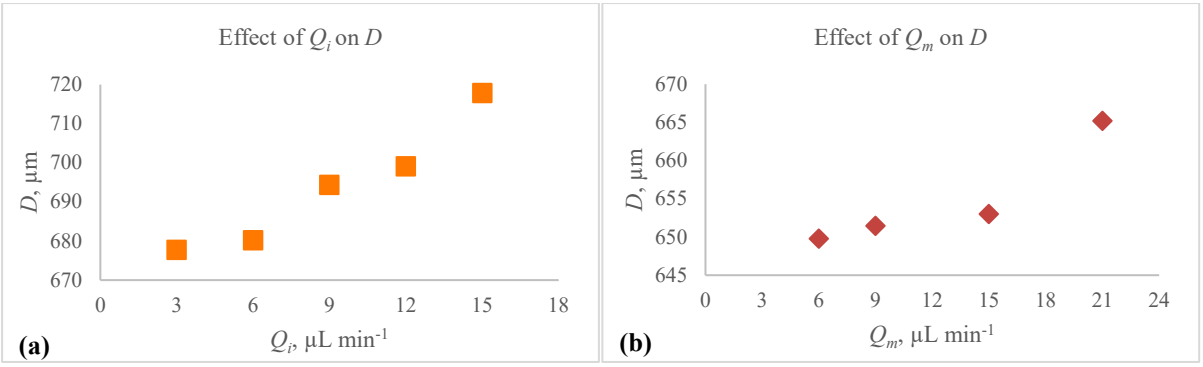

Fig. 2. Size of microcapsules increases with increasing Q_i or Q_m.

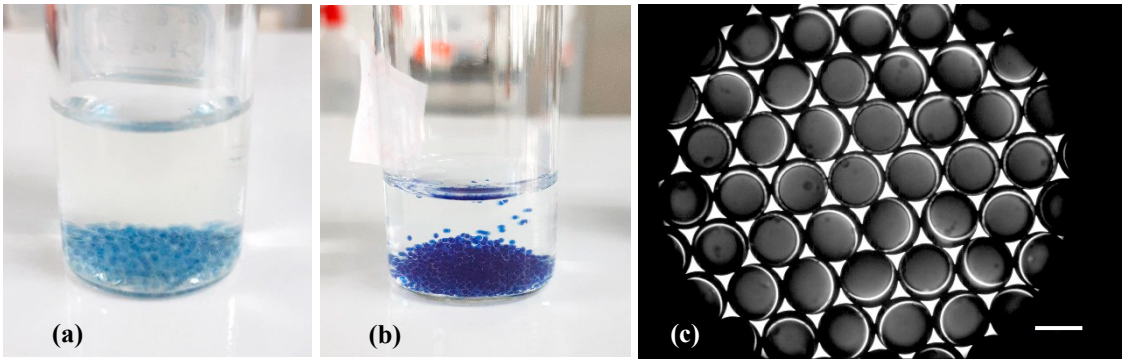

Fig. 3. Microencapsulated solvent with K_2CO_3 encapsulated in PDMS shell. The particles are cured and kept in vials for 3 months. Microcapsules in (a) are transferred and kept in vials with distilled water while microcapsules in (b) are kept in potassium carbonate solution isotonic to the core solvent. The microcapsules in (a) show signs of swelling, rupturing and dilution of core solution, which could be attributed to poor/insufficient curing of PDMS and swelling in pure water osmotically. (c) An optical image of microcapsules showing distinct core-shell layer. Scale bar is 500 μm.

The PDMS shell material used in this research paper is different from the UV curable shell used by Vericella, Nabavi and Wang's work, as PDMS is heat cured. Due to the microscopic size, curing of the PDMS microcapsules has been relatively fast through the transfer of heat using hot water. To avoid coalescence of capsules before they are solidified, Nabavi et al. added lipophilic stabilizers to the silicone rubber, however no stabilizer is added to PDMS, yet the microcapsules appeared to be stable throughout the curing process. Nabavi et al. conducted a comprehensive study on the solidification of the photocurable and determined that for optimal solidification, the microcapsules would have to UV irradiated 'on-the-fly' immediately after they are produced, else the microcapsules would collapse within 15 to 20 minutes upon collection, and subsequently the capsules would have to be left under irradiance for another 30 to 40 minutes to ensure complete curing. By comparison, PDMS is more cost-effective and PDMS microcapsules exhibited good stability. Upon curing, the microcapsules were stored in aqueous potassium carbonate isotonic to the liquid core to minimize osmotic imbalance leading to capsule swelling. In Figure 3 (a), the microcapsules are kept in distilled water in vials for 3 months long, and the capsules have shown signs of swelling and rupture whereas capsules in (b) are kept in 3 wt% aqueous potassium carbonate solution and did not show signs swelling or leaking.

The microcapsules are subjected to CO_2 absorption-desorption test in a customized apparatus such as that shown in Figure 4(c). The addition of thymol blue into the liquid core allows qualitative monitoring of capsule loading and unloading. On exposure to CO_2, the microcapsules turned gradually from blue to yellow, indicating absorption of CO_2 through the shell layer into the core containing 3 wt% K_2CO_3. The microcapsules were regenerated when nitrogen gas was channeled through the column, turning from yellow back to blue.

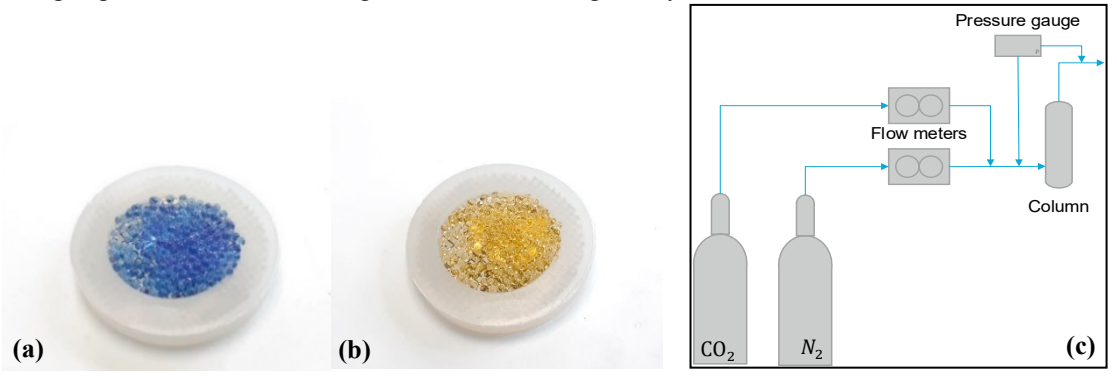

Fig. 4. Optical images of microcapsules containing 3 wt% potassium carbonate containing thymol blue indicator prior to exposure to CO_2 gas (a) and turning yellow after incubation in CO_2 gas (b). (c) Schematic of setup for absorption-desorption test.

5. Conclusion & Future work

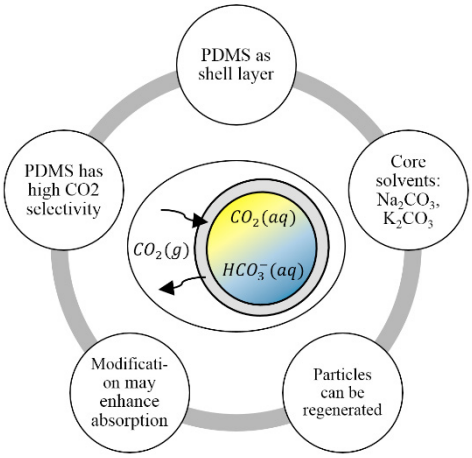

Fig. 5. Traits of microcapsules for carbon capture produced via needle-based microdevice.

This work primarily demonstrates the use of off-the-shelf needle-based microdevice for the production of microcapsules for carbon capture, a first of its kind application especially in environmental remediation. The needle device is an innovative design and has proven to be able to produce monodisperse functional microcapsules at low cost and good reliability. Arguably the production of monodisperse emulsions via the needle device is on a drop-by-drop basis which may result in low throughput, yet production rate may be increased through parallelization of devices and extension of microchannel networks.

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